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Two-dimensional hydrogen-bonded polymers in the crystal structures of the ammonium salts of phenoxyacetic acid, (4-fluorophenoxy)acetic acid and (4-chloro-2-methylphenoxy)acetic acid

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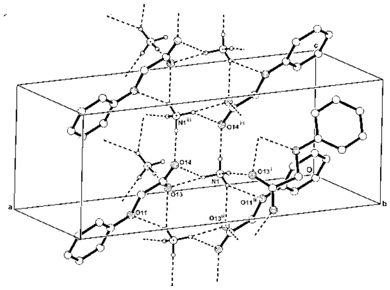
The structures of the ammonium salts of phenoxyacetic acid, $NH_4^+\cdot C_8H_6O_3^-$, (I), (4-fluorophenoxy)acetic acid, $NH_4^+\cdot C_8H_5FO_3^-$, (II), and the herbicidally active (4-chloro-2-methylphenoxy)acetic acid (MCPA), $NH_4^+\cdot C_9H_8ClO_3^-\cdot 0.5H_2O$, (III) have been determined. All have two-dimensional layered structures based on inter-species ammonium $N-H\cdots O$ hydrogen-bonding associations, which give core substructures consisting primarily of conjoined cyclic motifs. The crystals of (I) and (II) are isomorphous with the core comprising $R_1^2(5)$, $R_1^2(4)$ and centrosymmetric $R_4^2(8)$ ring motifs, giving two-dimensional layers lying parallel to (100). In (III), the water molecule of solvation lies on a crystallographic twofold rotation axis and bridges two carboxyl O atoms in an $R_4^4(12)$ hydrogen-bonded motif, creating two $R_4^3(10)$ rings, which together with a conjoined centrosymmetric $R_4^2(8)$ ring incorporating both ammonium cations, generate two-dimensional layers lying parallel to (100). No π–π ring associations are present in any of the structures.

Keywords: crystal structure; phenoxyacetic acid salts; MCPA; herbicides; ammonium carboxylates; hydrogen bonding

CCDC references: 1033945; 1033946; 1033947

Supporting information: this article has supporting information at journals.iucr.org/e

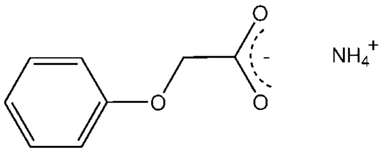


1. Chemical context

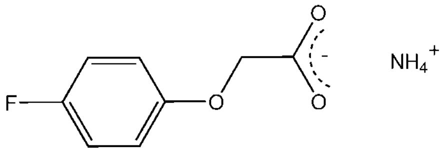
The crystal structures of the ammonium salts of carboxylic acids are, despite their simple formulae, characterized by the presence of a complex array of hydrogen-bonding interactions. From a study of the packing motifs of the these ammonium carboxylate salts from examples in the Cambridge Structural Database (Groom & Allen, 2014), Odendal *et al.* (2010) found that two-dimensional hydrogen-bonded nets, ladders or cubane-type structures could be predicted on the basis of the size and conformation of the anions. These structures are often stabilized by π–π aromatic ring interactions. With the benzoic acid analogues, two-dimensional sheet structures are common with interactions involving the ammonium cations and the carboxylate anions in $N-H\cdots O$ hydrogen bonding, forming core layer structures, with the aromatic rings occupying the interstitial cell regions, *e.g.* with benzoic acid (Odendal *et al.*, 2010), 3-nitrobenzoic acid (Eppel & Bernstein, 2009) and 2,4-dichlorobenzoic acid (Smith, 2014). Three-dimensional structures are usually only formed when interactive substituent groups are present on the benzoate rings, interlinking the layers *e.g.* with 3,5-dinitrobenzoic acid (Smith, 2014). The presence of water molecules of solvation may also produce a similar effect, although these are usually confined to the primary cation–anion layers.

With the phenoxyacetic acid analogues, which comprise a number of herbicidally active commercial herbicides

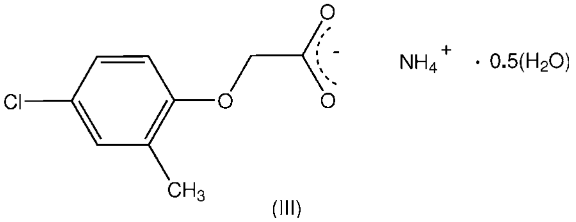
(Zumdahl, 2010), this should also be the case. In the only reported structure of an ammonium salt of a phenoxyacetic acid [with the commercially important herbicide, the 2,4-dichloro-substituted analogue (2,4-D) (a hemihydrate) (Liu *et al.*, 2009)], the expected two-dimensional layered structure is found. Herein are reported the preparation and structures of the anhydrous ammonium salts of the parent phenoxyacetic acid, $NH_4^+\cdot C_8H_6O_3^-$ (I) and (4-fluorophenoxy)acetic acid, $NH_4^+\cdot C_8H_5FO_3^-$ (II) and the hemihydrate salt of the herbicidally active (4-chloro-2-methylphenoxy)acetic acid (MCPA), $NH_4^+\cdot C_9H_8ClO_3^-\cdot 0.5H_2O$ (III). The structure of a hydrated chloromethylammonium salt of MCPA is known (Pernak *et al.*, 2011).



(I)



(II)



(III)

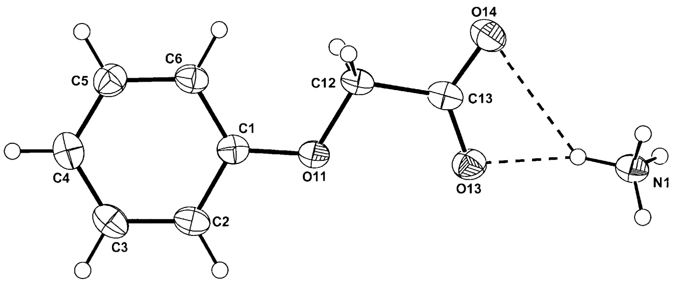


Figure 1
Molecular conformation and atom labelling for (I), with inter-species hydrogen bonds shown as a dashed lines (see Table 1 for details). Non-H atoms are shown as 40% probability displacement ellipsoids.

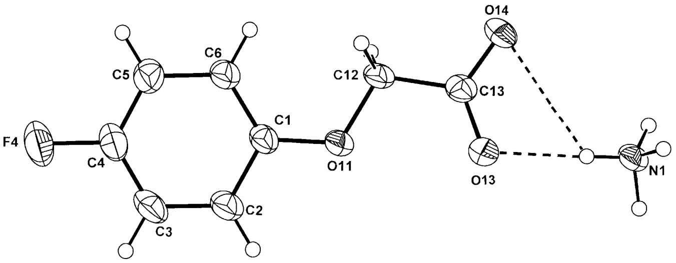


Figure 2
Molecular conformation and atom labelling for (II), with inter-species hydrogen bonds shown as dashed lines (see Table 2 for details). Non-H atoms are shown as 40% probability displacement ellipsoids.

2. Structural commentary

In the structures of the isomorphous ammonium phenoxyacetate (I) and (4-fluorophenoxy)acetate (II) (Figs. 1 and 2, respectively), the anionic species are essentially planar; the comparative defining torsion angles in the phenoxyacetate side chain (C2—C1—O11—C12, C1—O11—C12—C13 and O11—C12—C13—O14) are 178.93 (19), −177.48 (18) and −173.58 (18)°, respectively, for (I) and −179.05 (18), −178.98 (17) and −174.13 (17)°, respectively, for (II). This planarity is also found in the MCPA anion in (III) (Fig. 3) where the corresponding torsion angles are −179.13 (15), −173.34 (14) and −178.71 (15)° and is also the case with the parent acids [for (I): Kennard *et al.* (1982), for (II): Smith *et al.* (1992) and for (III): Smith & Kennard (1981); Sieron *et al.* (2011)]. In (III), the water molecule of solvation lies on a crystallographic twofold rotation axis.

3. Supramolecular features

In the crystals of (I) and (II), two H atoms of the ammonium group give cyclic asymmetric three-centre (bifurcated) N—H···(O,O) hydrogen-bonding interactions with the anion (Tables 1 and 2, respectively). One of these is with two O-atom acceptors of the carboxyl group (O13, O14) [graph set $R_1^2(4)$], the other is with the carboxyl and phenoxy O-atom acceptors (O13^{ii}, O11^{ii}) of an inversion-related anion [graph set $R_1^2(5)$]. These, together with a third N1—H13···O13^{ii} hydrogen bond, give a cyclic $R_4^2(8)$ ring motif, forming a series of conjoined rings which extend the structures along *c*. The other H atom gives structure extension through an N—H···O hydrogen bond to a carboxyl O atom (O14^{iii}), forming a two-dimensional sheet-like structure which lies parallel to (100). Present in the crystal are short inversion-related intermolecular F4···F4^{iv} contacts of 2.793 (2) Å [symmetry code: (iv) $-x + 2$,

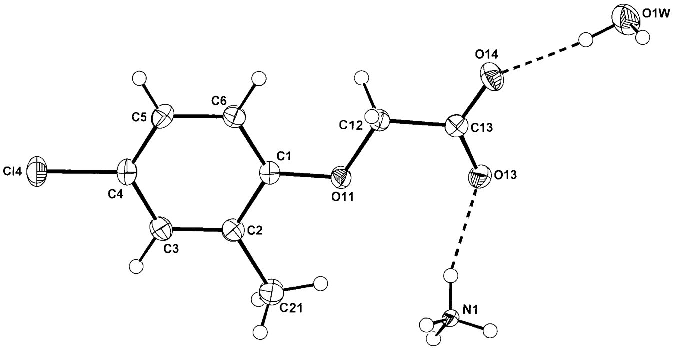


Figure 3
Molecular conformation and atom labelling for (III), with inter-species hydrogen bonds shown as dashed lines (see Table 3 for details). Non-H atoms are shown as 40% probability displacement ellipsoids.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H11⋯O13	0.96	1.92	2.849 (3)	163
N1—H11⋯O14	0.96	2.55	3.330 (3)	138
N1—H12⋯O13^{i}	0.85	2.03	2.867 (3)	172
N1—H13⋯O11^{ii}	0.90	2.39	3.202 (3)	150
N1—H13⋯O13^{ii}	0.90	2.15	2.869 (3)	136
N1—H14⋯O14^{iii}	0.84	1.95	2.788 (3)	178

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H11⋯O13	0.90	1.95	2.847 (2)	177
N1—H11⋯O14	0.90	2.55	3.347 (2)	135
N1—H12⋯O13^{i}	0.97	1.88	2.847 (3)	173
N1—H13⋯O11^{ii}	0.96	2.36	3.172 (2)	142
N1—H13⋯O13^{ii}	0.96	2.13	2.892 (2)	135
N1—H14⋯O14^{iii}	0.89	1.91	2.793 (2)	173

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H11⋯O13^{i}	0.82	2.21	2.998 (4)	161
N1—H12⋯O14^{ii}	0.82	2.09	2.886 (4)	166
N1—H13⋯O13^{iii}	0.84	2.04	2.877 (4)	173
N1—H14⋯O13	0.82	2.00	2.798 (4)	163
O1*W*—H11*W*⋯O14	0.88	1.95	2.809 (4)	165

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x, -y+2, z-\frac{1}{2}$; (iii) $x, y-1, z$.

$-y+1, -z-1$]. The crystal packing and hydrogen-bonding in (I) is identical to that in isostructural (II), as shown in Fig. 4.

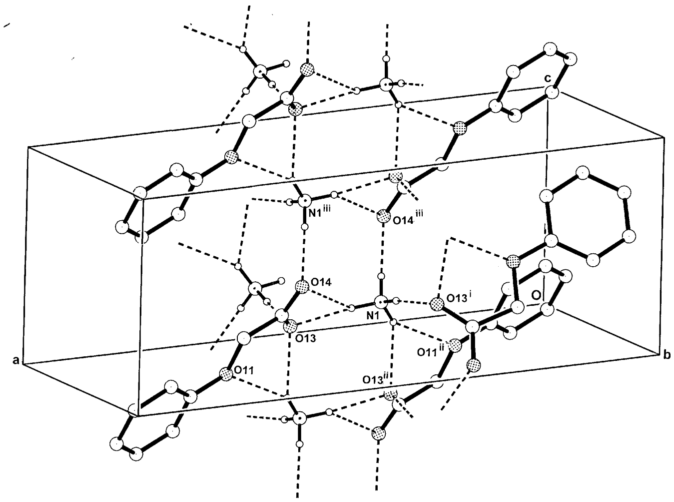


Figure 4
The two-dimensional hydrogen-bonded network structure of (I), which is equivalent to that of the isomorphous compound (II). Hydrogen bonds are shown as dashed lines and non-associative H-atoms have been omitted [for symmetry codes see Tables 1 and 2].

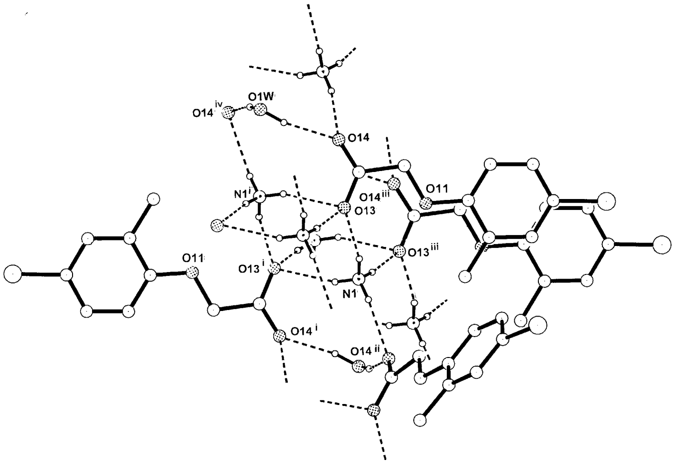


Figure 5
A partial extension of the basic cation–anion hydrogen-bonding associations in the structure of (III), showing conjoined cyclic $R_4^4(12)$, $R_4^3(10)$ and $R_4^2(8)$ ring motifs. [Symmetry code: (iv) $-x+1, y, -z+\frac{3}{2}$. For other codes, see Table 3].

In the crystal of (III), centrosymmetric inter-ion $R_4^2(8)$ rings are formed between two ammonium cations and two O13 carboxyl O-atom acceptors and are bridged by a third ammonium H donor through O13^{iii}, extending the structure down *b* (Table 3 and Fig. 5). The fourth H atom gives extension along *a* through N1—H12⋯O14^{ii} forming an enlarged conjoined $R_4^4(12)$ ring, which is bridged by the water molecule of solvation lying on the twofold rotation axis, through O1*W*—H11*W*⋯O14 hydrogen bonds. This link effectively generates two separate $R_4^3(10)$ ring motifs, extending the structure along *a* and giving the overall two-dimensional layers lying parallel to (100) (Fig. 6). In (III), no three-centre $R_1^2(4)$ or $R_1^2(5)$ motifs to carboxyl (O,O') or carboxyl-phenoxy (O,O^1) acceptors such as are present in (I) and (II) are found. The structure of (III) is essentially isostructural with that of ammonium (2,4-dichlorophenoxy)acetate hemihydrate (Liu *et al.*, 2009), with isomorphous crystals [a = 37.338 (8), b = 4.388 (9), c = 12.900 (3) Å, β = 103.82 (3)°, V = 2074.7 (8) Å^3, Z = 8, space group $C2/c$].

No π–π interactions are found in any of the structures reported here [minimum ring centroid separation = 4.8849 (16) (I), 4.8919 (15) (II) and 4.456 (5) Å (III) (the *b* unit-cell parameter)].

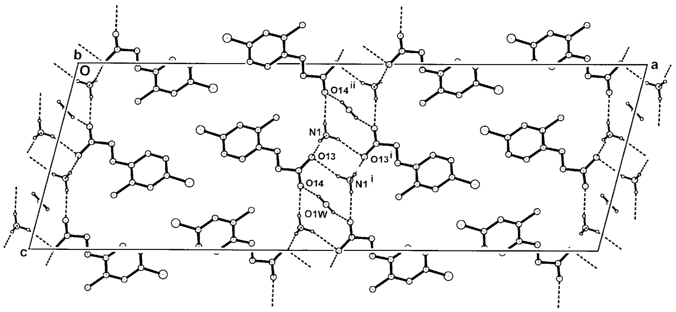


Figure 6
The two-dimensional hydrogen-bonded network structure of (III) in the unit cell, viewed along *b*.

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$NH_4^+ \cdot C_8H_7O_3^-$	$NH_4^+ \cdot C_8H_6FO_3^-$	$NH_4^+ \cdot C_9H_8ClNO_3^- \cdot 0.5H_2O$
M_r	169.17	187.17	226.65
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Temperature (K)	200	200	200
a, b, c (Å)	17.824 (2), 7.1453 (6), 6.7243 (7)	18.386 (2), 7.1223 (6), 6.7609 (6)	38.0396 (9), 4.4560 (8), 12.944 (5)
β (°)	90.321 (9)	93.399 (8)	104.575 (5)
V (Å^3)	856.38 (15)	883.79 (14)	2123.5 (9)
Z	4	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.10	0.12	0.35
Crystal size (mm)	0.35 × 0.25 × 0.10	0.26 × 0.20 × 0.05	0.35 × 0.35 × 0.10
Data collection			
Diffractometer	Oxford Diffraction Gemini-S CCD detector	Oxford Diffraction Gemini-S CCD detector	Oxford Diffraction Gemini-S CCD detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)	Multi-scan (*CrysAlis PRO*; Agilent, 2013)	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.920, 0.980	0.960, 0.980	0.913, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5450, 1686, 1218	5619, 1738, 1304	6215, 2087, 1771
R_{int}	0.052	0.033	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617	0.617
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.163, 1.10	0.053, 0.116, 1.10	0.036, 0.091, 1.03
No. of reflections	1686	1738	2087
No. of parameters	109	118	132
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.24	0.16, −0.22	0.32, −0.28

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SIR92* (Altomare *et al.*, 1993), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

4. Synthesis and crystallization

The title compounds were prepared by the addition of excess 5 *M* aqueous ammonia solution to 1 mmol of either phenoxyacetic acid [150 mg for (I)], (4-fluorophenoxy)acetic acid [170 mg for (II)] or (4-chloro-2-methylphenoxy)acetic acid [200 mg for (III)] in 10 mL of 10% ethanol–water. Room-temperature evaporation of the solvent gave colourless plate-like crystals of (I), (II) and (III) from which specimens were cleaved for the X-ray analyses.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located in difference Fourier maps but were subsequently included in the refinements with positional parameters fixed and with $U_{iso}(H) = 1.2U_{eq}(N)$ or $= 1.5U_{eq}(O)$. Other H atoms were included at calculated positions [C—H(aromatic) = 0.95, C—H(methylene) = 0.98, C—H(methyl) = 0.97 Å] and also treated as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $= 1.2U_{eq}(C)$ for other H atoms. In (III), the methyl group was found to be rotationally disordered, with the H atoms distributed over six equivalent half-sites, and was treated accordingly.

Acknowledgements

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supporting information

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Two-dimensional hydrogen-bonded polymers in the crystal structures of the ammonium salts of phenoxyacetic acid, (4-fluorophenoxy)acetic acid and (4-chloro-2-methylphenoxy)acetic acid

Graham Smith

Computing details

For all compounds, data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993) for (I); *SHELXS97* (Sheldrick, 2008) for (II), (III). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

(I) Ammonium phenoxyacetate

Crystal data

$NH_4^+\cdot C_8H_7O_3^-$
M_r = 169.17
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 17.824 (2) Å
b = 7.1453 (6) Å
c = 6.7243 (7) Å
β = 90.321 (9)°
V = 856.38 (15) Å^3
Z = 4
F(000) = 360
D_x = 1.312 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1041 reflections
θ = 3.4–25.5°
μ = 0.10 mm^{-1}
T = 200 K
Plate, colourless
0.35 × 0.25 × 0.10 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.920, T_{max} = 0.980
5450 measured reflections
1686 independent reflections
1218 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 26.0°, θ_{min} = 3.4°
$h = -21\rightarrow21$
$k = -8\rightarrow8$
$l = -8\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.163
S = 1.10
1686 reflections
109 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.1562P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O11	0.71681 (10)	0.4894 (2)	−0.0073 (2)	0.0357 (6)
O13	0.58441 (10)	0.4403 (2)	0.1635 (3)	0.0393 (6)
O14	0.60999 (11)	0.6471 (2)	0.4025 (3)	0.0444 (7)
C1	0.78672 (14)	0.4998 (3)	−0.0880 (4)	0.0317 (8)
C2	0.79737 (16)	0.4028 (3)	−0.2662 (4)	0.0373 (9)
C3	0.86706 (17)	0.3999 (4)	−0.3531 (4)	0.0436 (10)
C4	0.92709 (16)	0.4938 (4)	−0.2672 (4)	0.0429 (9)
C5	0.91570 (16)	0.5934 (3)	−0.0933 (4)	0.0404 (9)
C6	0.84634 (14)	0.5982 (3)	−0.0039 (4)	0.0358 (9)
C12	0.70534 (14)	0.5849 (3)	0.1764 (3)	0.0329 (8)
C13	0.62684 (15)	0.5544 (3)	0.2524 (3)	0.0331 (8)
N1	0.43517 (12)	0.5486 (3)	0.2601 (3)	0.0355 (7)
H2	0.75650	0.33900	−0.32710	0.0450*
H3	0.87410	0.33280	−0.47350	0.0530*
H4	0.97530	0.48990	−0.32670	0.0520*
H5	0.95640	0.65960	−0.03470	0.0480*
H6	0.83930	0.66830	0.11460	0.0430*
H121	0.71410	0.72050	0.15720	0.0390*
H122	0.74200	0.53900	0.27630	0.0390*
H11	0.48820	0.53280	0.24260	0.0430*
H12	0.43220	0.66300	0.29220	0.0430*
H13	0.40580	0.52630	0.15370	0.0430*
H14	0.42230	0.48720	0.36110	0.0430*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0366 (11)	0.0331 (10)	0.0373 (10)	−0.0020 (7)	0.0004 (8)	−0.0089 (7)
O13	0.0446 (12)	0.0323 (9)	0.0409 (10)	−0.0068 (8)	0.0011 (8)	−0.0014 (8)
O14	0.0571 (13)	0.0391 (11)	0.0370 (10)	−0.0059 (9)	0.0093 (9)	−0.0052 (8)
C1	0.0372 (15)	0.0228 (12)	0.0350 (13)	0.0037 (10)	−0.0040 (11)	0.0015 (10)

C2	0.0495 (17)	0.0276 (13)	0.0348 (14)	0.0010 (11)	−0.0030 (11)	−0.0032 (10)
C3	0.057 (2)	0.0359 (14)	0.0380 (15)	0.0056 (13)	0.0059 (13)	−0.0035 (11)
C4	0.0421 (18)	0.0421 (16)	0.0446 (15)	0.0049 (12)	0.0084 (12)	0.0030 (12)
C5	0.0405 (17)	0.0339 (14)	0.0468 (16)	−0.0016 (11)	−0.0018 (12)	−0.0002 (11)
C6	0.0424 (17)	0.0296 (13)	0.0355 (14)	0.0025 (10)	−0.0024 (11)	−0.0042 (10)
C12	0.0410 (16)	0.0279 (12)	0.0299 (13)	0.0008 (10)	−0.0024 (11)	−0.0049 (10)
C13	0.0496 (17)	0.0224 (12)	0.0273 (12)	0.0001 (11)	−0.0025 (11)	0.0039 (10)
N1	0.0434 (14)	0.0305 (11)	0.0325 (11)	−0.0006 (9)	−0.0014 (9)	−0.0023 (9)

Geometric parameters (Å, º)

O11—C1	1.364 (3)	C3—C4	1.386 (4)
O11—C12	1.427 (2)	C4—C5	1.385 (4)
O13—C13	1.261 (3)	C5—C6	1.378 (4)
O14—C13	1.245 (3)	C12—C13	1.508 (4)
N1—H12	0.8500	C2—H2	0.9500
N1—H13	0.9000	C3—H3	0.9500
N1—H14	0.8400	C4—H4	0.9500
N1—H11	0.9600	C5—H5	0.9500
C1—C6	1.392 (3)	C6—H6	0.9500
C1—C2	1.398 (4)	C12—H121	0.9900
C2—C3	1.376 (4)	C12—H122	0.9900

C1—O11—C12	117.00 (18)	O13—C13—O14	125.6 (2)
H12—N1—H14	106.00	O13—C13—C12	119.21 (19)
H13—N1—H14	113.00	C3—C2—H2	120.00
H11—N1—H12	102.00	C1—C2—H2	120.00
H11—N1—H13	117.00	C2—C3—H3	120.00
H11—N1—H14	108.00	C4—C3—H3	120.00
H12—N1—H13	110.00	C5—C4—H4	121.00
O11—C1—C6	124.3 (2)	C3—C4—H4	121.00
C2—C1—C6	119.5 (2)	C6—C5—H5	119.00
O11—C1—C2	116.3 (2)	C4—C5—H5	119.00
C1—C2—C3	119.9 (2)	C1—C6—H6	120.00
C2—C3—C4	120.8 (3)	C5—C6—H6	120.00
C3—C4—C5	119.0 (3)	H121—C12—H122	108.00
C4—C5—C6	121.2 (2)	O11—C12—H121	109.00
C1—C6—C5	119.7 (2)	O11—C12—H122	109.00
O11—C12—C13	111.22 (18)	C13—C12—H121	109.00
O14—C13—C12	115.2 (2)	C13—C12—H122	109.00

C12—O11—C1—C2	178.93 (19)	C1—C2—C3—C4	−0.7 (4)
C12—O11—C1—C6	−0.7 (3)	C2—C3—C4—C5	−0.9 (4)
C1—O11—C12—C13	−177.48 (18)	C3—C4—C5—C6	0.9 (4)
O11—C1—C2—C3	−177.4 (2)	C4—C5—C6—C1	0.7 (4)
C6—C1—C2—C3	2.3 (4)	O11—C12—C13—O13	6.7 (3)
O11—C1—C6—C5	177.3 (2)	O11—C12—C13—O14	−173.58 (18)
C2—C1—C6—C5	−2.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O13	0.96	1.92	2.849 (3)	163
N1—H11···O14	0.96	2.55	3.330 (3)	138
N1—H12···O13^{i}	0.85	2.03	2.867 (3)	172
N1—H13···O11^{ii}	0.90	2.39	3.202 (3)	150
N1—H13···O13^{ii}	0.90	2.15	2.869 (3)	136
N1—H14···O14^{iii}	0.84	1.95	2.788 (3)	178

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*+1, −*y*+1, −*z*+1.

(II) Ammonium (4-fluorophenoxy)acetate

Crystal data

$NH_4^+\cdot C_8H_6FO_3^-$
M_r = 187.17
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 18.386 (2) Å
b = 7.1223 (6) Å
c = 6.7609 (6) Å
β = 93.399 (8)°
V = 883.79 (14) Å^3
Z = 4
F(000) = 392
D_x = 1.407 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1311 reflections
θ = 3.3–28.0°
μ = 0.12 mm^{-1}
T = 200 K
Plate, colourless
0.26 × 0.20 × 0.05 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.960, T_{max} = 0.980
5619 measured reflections
1738 independent reflections
1304 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.0°, θ_{min} = 3.1°
h = −22→20
k = −8→8
l = −7→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.116
S = 1.10
1738 reflections
118 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.2467P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
F4	0.97409 (8)	0.4959 (2)	−0.3100 (2)	0.0761 (6)
O11	0.70924 (8)	0.4850 (2)	0.0189 (2)	0.0451 (5)
O13	0.58131 (8)	0.4391 (2)	0.1749 (2)	0.0439 (5)
O14	0.60820 (8)	0.6448 (2)	0.4167 (2)	0.0504 (6)
C1	0.77687 (12)	0.4984 (3)	−0.0575 (3)	0.0409 (8)
C2	0.78437 (13)	0.4048 (3)	−0.2361 (3)	0.0487 (8)
C3	0.85114 (14)	0.4052 (4)	−0.3198 (3)	0.0548 (9)
C4	0.90870 (13)	0.4967 (4)	−0.2263 (4)	0.0529 (9)
C5	0.90226 (13)	0.5918 (4)	−0.0520 (3)	0.0520 (9)
C6	0.83562 (12)	0.5925 (3)	0.0333 (3)	0.0463 (8)
C12	0.69955 (11)	0.5819 (3)	0.2002 (3)	0.0411 (7)
C13	0.62335 (12)	0.5521 (3)	0.2684 (3)	0.0382 (7)
N1	0.43689 (9)	0.5487 (3)	0.2527 (2)	0.0417 (6)
H2	0.74400	0.34140	−0.29970	0.0580*
H3	0.85700	0.34210	−0.44160	0.0660*
H5	0.94280	0.65620	0.00930	0.0620*
H6	0.83020	0.65760	0.15420	0.0560*
H121	0.70810	0.71780	0.18130	0.0490*
H122	0.73570	0.53600	0.30340	0.0490*
H11	0.48210	0.50970	0.22990	0.0500*
H12	0.42870	0.67850	0.28670	0.0500*
H13	0.40960	0.51140	0.13330	0.0500*
H14	0.42010	0.48100	0.35030	0.0500*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F4	0.0554 (10)	0.1149 (13)	0.0604 (10)	0.0161 (9)	0.0230 (8)	0.0035 (9)
O11	0.0373 (9)	0.0661 (11)	0.0316 (8)	0.0035 (7)	0.0001 (6)	−0.0140 (7)
O13	0.0428 (9)	0.0527 (9)	0.0362 (9)	−0.0041 (7)	0.0034 (7)	−0.0052 (7)
O14	0.0585 (11)	0.0630 (10)	0.0308 (9)	−0.0037 (8)	0.0115 (7)	−0.0097 (8)
C1	0.0382 (13)	0.0554 (14)	0.0291 (12)	0.0110 (10)	0.0012 (9)	−0.0016 (10)
C2	0.0517 (15)	0.0630 (16)	0.0312 (12)	0.0072 (12)	0.0009 (10)	−0.0062 (11)
C3	0.0636 (17)	0.0717 (17)	0.0298 (12)	0.0147 (14)	0.0085 (11)	−0.0051 (12)
C4	0.0437 (15)	0.0744 (17)	0.0416 (14)	0.0159 (13)	0.0114 (11)	0.0054 (12)
C5	0.0397 (14)	0.0719 (17)	0.0441 (14)	0.0070 (12)	0.0002 (11)	0.0013 (12)
C6	0.0398 (13)	0.0651 (16)	0.0338 (12)	0.0072 (11)	−0.0006 (10)	−0.0073 (11)
C12	0.0409 (13)	0.0565 (14)	0.0253 (11)	0.0054 (11)	−0.0033 (9)	−0.0088 (10)
C13	0.0432 (13)	0.0445 (12)	0.0263 (11)	0.0034 (10)	−0.0019 (9)	0.0032 (10)
N1	0.0438 (11)	0.0555 (12)	0.0257 (9)	0.0053 (9)	0.0024 (8)	−0.0060 (8)

Geometric parameters (Å, º)

F4—C4	1.359 (3)	C2—C3	1.382 (3)
O11—C1	1.378 (3)	C3—C4	1.366 (4)
O11—C12	1.427 (2)	C4—C5	1.370 (4)
O13—C13	1.260 (3)	C5—C6	1.385 (3)
O14—C13	1.246 (2)	C12—C13	1.516 (3)
N1—H13	0.9600	C2—H2	0.9500
N1—H14	0.8900	C3—H3	0.9500
N1—H11	0.9000	C5—H5	0.9500
N1—H12	0.9700	C6—H6	0.9500
C1—C6	1.384 (3)	C12—H121	0.9900
C1—C2	1.393 (3)	C12—H122	0.9900
C1—O11—C12	116.74 (16)	O11—C12—C13	111.00 (16)
H12—N1—H14	106.00	O13—C13—O14	125.6 (2)
H13—N1—H14	107.00	O14—C13—C12	115.18 (18)
H11—N1—H12	120.00	O13—C13—C12	119.18 (18)
H11—N1—H13	102.00	C1—C2—H2	120.00
H11—N1—H14	109.00	C3—C2—H2	120.00
H12—N1—H13	113.00	C4—C3—H3	120.00
O11—C1—C6	124.43 (18)	C2—C3—H3	120.00
C2—C1—C6	120.1 (2)	C6—C5—H5	121.00
O11—C1—C2	115.45 (19)	C4—C5—H5	121.00
C1—C2—C3	119.3 (2)	C1—C6—H6	120.00
C2—C3—C4	119.6 (2)	C5—C6—H6	120.00
C3—C4—C5	122.0 (2)	H121—C12—H122	108.00
F4—C4—C3	119.1 (2)	O11—C12—H121	109.00
F4—C4—C5	118.9 (2)	O11—C12—H122	109.00
C4—C5—C6	118.9 (2)	C13—C12—H121	109.00
C1—C6—C5	120.0 (2)	C13—C12—H122	109.00
C12—O11—C1—C2	−179.05 (18)	C2—C3—C4—F4	179.9 (2)
C12—O11—C1—C6	2.5 (3)	C2—C3—C4—C5	−1.1 (4)
C1—O11—C12—C13	−178.98 (17)	F4—C4—C5—C6	−180.0 (2)
O11—C1—C2—C3	−177.7 (2)	C3—C4—C5—C6	1.0 (4)
C6—C1—C2—C3	0.8 (3)	C4—C5—C6—C1	−0.1 (4)
O11—C1—C6—C5	177.5 (2)	O11—C12—C13—O13	6.0 (3)
C2—C1—C6—C5	−0.8 (3)	O11—C12—C13—O14	−174.13 (17)
C1—C2—C3—C4	0.2 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O13	0.90	1.95	2.847 (2)	177
N1—H11···O14	0.90	2.55	3.347 (2)	135
N1—H12···O13$^{\mathrm{i}}$	0.97	1.88	2.847 (3)	173
N1—H13···O11$^{\mathrm{ii}}$	0.96	2.36	3.172 (2)	142

N1—H13···O13^{ii}	0.96	2.13	2.892 (2)	135
N1—H14···O14^{iii}	0.89	1.91	2.793 (2)	173

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*+1, −*y*+1, −*z*+1.

(III) Ammonium (4-chloro-2-methylphenoxy)acetate hemihydrate

Crystal data

$NH_4^+\cdot C_9H_8ClNO_3^-\cdot 0.5H_2O$
M_r = 226.65
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 38.0396 (9) Å
b = 4.4560 (8) Å
c = 12.944 (5) Å
β = 104.575 (5)°
V = 2123.5 (9) Å^3
Z = 8
$F(000)$ = 952
D_x = 1.418 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 1819 reflections
θ = 4.4–28.1°
μ = 0.35 mm^{-1}
T = 200 K
Plate, colourless
0.35 × 0.35 × 0.10 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.913, T_{max} = 0.980
6215 measured reflections
2087 independent reflections
1771 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 26.0°, θ_{min} = 3.2°
h = −46→46
k = −5→5
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.091
S = 1.03
2087 reflections
132 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.4504P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl4	0.24818 (1)	0.32330 (12)	0.36021 (4)	0.0372 (2)	

O11	0.39197 (3)	0.8996 (3)	0.46961 (9)	0.0262 (4)	
O13	0.45425 (3)	1.2161 (3)	0.49906 (10)	0.0296 (4)	
O14	0.44789 (4)	1.4021 (3)	0.65332 (10)	0.0339 (4)	
C1	0.35808 (5)	0.7686 (4)	0.44981 (13)	0.0224 (5)	
C2	0.34876 (5)	0.5869 (4)	0.35836 (13)	0.0246 (5)	
C3	0.31491 (5)	0.4496 (4)	0.33324 (14)	0.0269 (5)	
C4	0.29091 (5)	0.4918 (4)	0.39679 (14)	0.0264 (5)	
C5	0.30027 (5)	0.6675 (4)	0.48684 (14)	0.0275 (6)	
C6	0.33390 (5)	0.8070 (4)	0.51321 (14)	0.0258 (5)	
C12	0.40205 (5)	1.0812 (4)	0.56298 (14)	0.0242 (5)	
C13	0.43762 (5)	1.2444 (4)	0.57156 (14)	0.0234 (5)	
C21	0.37517 (5)	0.5430 (5)	0.29002 (15)	0.0370 (6)	
O1W	0.50000	1.8306 (4)	0.75000	0.0464 (7)	
N1	0.46781 (3)	0.7274 (3)	0.37900 (10)	0.0156 (4)	
H3	0.30820	0.32800	0.27310	0.0320*	
H5	0.28420	0.69260	0.52960	0.0330*	
H6	0.34030	0.92710	0.57380	0.0310*	
H121	0.40420	0.95550	0.62550	0.0290*	
H122	0.38300	1.22720	0.56190	0.0290*	
H211	0.39700	0.65450	0.31980	0.0550*	0.500
H212	0.36440	0.61300	0.21890	0.0550*	0.500
H213	0.38090	0.33380	0.28790	0.0550*	0.500
H214	0.36460	0.41300	0.23130	0.0550*	0.500
H215	0.39710	0.45450	0.33210	0.0550*	0.500
H216	0.38060	0.73370	0.26320	0.0550*	0.500
H11W	0.48390	1.71260	0.70860	0.0700*	
H11	0.49010	0.73870	0.39810	0.0190*	
H12	0.45970	0.71470	0.31450	0.0190*	
H13	0.46250	0.57360	0.40950	0.0190*	
H14	0.45930	0.86670	0.40680	0.0190*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl4	0.0264 (3)	0.0466 (3)	0.0378 (3)	−0.0121 (2)	0.0064 (2)	−0.0044 (2)
O11	0.0233 (7)	0.0335 (7)	0.0230 (6)	−0.0071 (5)	0.0083 (5)	−0.0075 (5)
O13	0.0293 (7)	0.0279 (6)	0.0355 (7)	−0.0036 (6)	0.0155 (6)	−0.0015 (6)
O14	0.0340 (8)	0.0378 (7)	0.0268 (7)	−0.0094 (6)	0.0020 (6)	−0.0054 (6)
C1	0.0215 (9)	0.0222 (8)	0.0224 (9)	−0.0010 (7)	0.0037 (7)	0.0028 (7)
C2	0.0253 (9)	0.0277 (9)	0.0198 (8)	0.0005 (7)	0.0041 (7)	0.0002 (7)
C3	0.0278 (10)	0.0287 (9)	0.0223 (9)	−0.0021 (8)	0.0027 (8)	−0.0023 (8)
C4	0.0217 (9)	0.0277 (9)	0.0277 (9)	−0.0031 (7)	0.0023 (8)	0.0037 (8)
C5	0.0230 (10)	0.0332 (10)	0.0282 (9)	0.0003 (8)	0.0099 (8)	0.0017 (8)
C6	0.0259 (10)	0.0281 (9)	0.0234 (9)	−0.0011 (8)	0.0062 (7)	−0.0022 (8)
C12	0.0244 (9)	0.0276 (9)	0.0208 (8)	−0.0026 (7)	0.0059 (7)	−0.0033 (7)
C13	0.0247 (9)	0.0215 (8)	0.0232 (9)	0.0029 (7)	0.0045 (7)	0.0042 (7)
C21	0.0331 (11)	0.0520 (12)	0.0278 (10)	−0.0083 (10)	0.0114 (9)	−0.0126 (9)
O1W	0.0421 (13)	0.0259 (10)	0.0667 (15)	0.0000	0.0053 (11)	0.0000

N1	0.0141 (7)	0.0159 (6)	0.0179 (6)	−0.0006 (5)	0.0060 (5)	−0.0004 (5)

Geometric parameters (Å, º)

Cl4—C4	1.744 (3)	C3—C4	1.387 (3)
O11—C1	1.379 (3)	C4—C5	1.375 (3)
O11—C12	1.425 (3)	C5—C6	1.386 (3)
O13—C13	1.263 (3)	C12—C13	1.515 (3)
O14—C13	1.248 (3)	C3—H3	0.9300
O1W—H11W	0.8800	C5—H5	0.9300
O1W—H11W^{i}	0.8800	C6—H6	0.9300
N1—H12	0.8200	C12—H121	0.9700
N1—H11	0.8200	C12—H122	0.9700
N1—H13	0.8400	C21—H216	0.9600
N1—H14	0.8200	C21—H211	0.9600
C1—C2	1.404 (3)	C21—H212	0.9600
C1—C6	1.389 (3)	C21—H213	0.9600
C2—C21	1.509 (3)	C21—H214	0.9600
C2—C3	1.388 (3)	C21—H215	0.9600
C1—O11—C12	115.95 (13)	C2—C3—H3	120.00
H11W—O1W—H11W^{i}	107.00	C4—C3—H3	120.00
H12—N1—H14	114.00	C4—C5—H5	120.00
H13—N1—H14	104.00	C6—C5—H5	120.00
H11—N1—H12	114.00	C5—C6—H6	120.00
H11—N1—H13	105.00	C1—C6—H6	120.00
H11—N1—H14	108.00	C13—C12—H122	109.00
H12—N1—H13	111.00	C13—C12—H121	109.00
O11—C1—C2	115.26 (16)	O11—C12—H121	109.00
O11—C1—C6	124.41 (15)	O11—C12—H122	109.00
C2—C1—C6	120.33 (17)	H121—C12—H122	108.00
C1—C2—C21	120.32 (17)	C2—C21—H211	109.00
C1—C2—C3	118.30 (17)	C2—C21—H212	109.00
C3—C2—C21	121.37 (16)	C2—C21—H213	109.00
C2—C3—C4	120.77 (16)	C2—C21—H214	110.00
C3—C4—C5	120.76 (18)	C2—C21—H215	109.00
Cl4—C4—C3	119.22 (14)	C2—C21—H216	109.00
Cl4—C4—C5	120.01 (15)	H214—C21—H215	109.00
C4—C5—C6	119.37 (17)	H214—C21—H216	109.00
C1—C6—C5	120.46 (16)	H215—C21—H216	110.00
O11—C12—C13	112.31 (15)	H211—C21—H212	109.00
O13—C13—O14	125.29 (18)	H211—C21—H213	110.00
O13—C13—C12	120.17 (16)	H212—C21—H213	109.00
O14—C13—C12	114.55 (16)		
C12—O11—C1—C2	−179.13 (15)	C1—C2—C3—C4	0.2 (3)
C12—O11—C1—C6	1.0 (2)	C21—C2—C3—C4	179.98 (17)
C1—O11—C12—C13	−173.34 (14)	C2—C3—C4—Cl4	178.25 (14)

O11—C1—C2—C3	−179.57 (15)	C2—C3—C4—C5	−0.8 (3)
O11—C1—C2—C21	0.6 (2)	Cl4—C4—C5—C6	−178.13 (14)
C6—C1—C2—C3	0.3 (3)	C3—C4—C5—C6	0.9 (3)
C6—C1—C2—C21	−179.46 (17)	C4—C5—C6—C1	−0.4 (3)
O11—C1—C6—C5	179.67 (16)	O11—C12—C13—O13	1.7 (2)
C2—C1—C6—C5	−0.2 (3)	O11—C12—C13—O14	−178.71 (15)

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O13^{ii}	0.82	2.21	2.998 (4)	161
N1—H12···O14^{iii}	0.82	2.09	2.886 (4)	166
N1—H13···O13^{iv}	0.84	2.04	2.877 (4)	173
N1—H14···O13	0.82	2.00	2.798 (4)	163
O1*W*—H11*W*···O14	0.88	1.95	2.809 (4)	165

Symmetry codes: (ii) $-x+1, -y+2, -z+1$; (iii) $x, -y+2, z-1/2$; (iv) $x, y-1, z$.